

Referee's report on PhD thesis

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Novel conjugated polymers of the metallo-supramolecular and polyelectrolyte class

The presented thesis deals with the development of conjugated polymers with improved processability from solutions. Two types of ionic polymers were prepared and characterized: (a) conjugated metallo-supramolecular polymers (MSP) containing new heteroaromatic unimers capable of binding to metal ions and form the charged polymer chain, (b) polythiophene polyelectrolytes containing positively charged pendant groups. Due to their charged nature, both types of the polymers are soluble in water and polar solvents (alcohols, DMSO). Moreover, the MSPs have the advantage of easy control of their length by choice of solvents, temperature and the ratio of metal cations and unimers.

The thesis is written clearly, following the standard structure, and besides the text itself (99 pages) also contains as attachments full texts of four published papers related to this work. The theoretical part of the thesis describes sufficiently the present status in the area of MSP, conjugated polymers and polyelectrolytes, citing close to 200 relevant publications. The Results part is divided into the two main sections, first describing MSP: multistep synthesis and characterization of new types of unimers (based on bis(imidazolyl)pyridine and bis(oxazoliny)pyridine - pybox), preparation of MSP using pybox unimer and several cations, studying the properties of MSPs depending on the ratio Mt^{2+} /unimer using UV/Vis, luminescence spectra – their dyanmer properties were confirmed. The second section of Results deals with preparation of covalent phosphonium polythiophene polyelectrolytes studies their properties depending on their regioregularity and makes reasonable conclusions. In the Experimental part are well described all procedures used in the experiments and all new compounds reasonably well characterized (1H , ^{13}C NMR, IR, elemental analysis).

Nevertheless, I have some comments and recommendations for the author:

- The name “oxazole” is used several times wrongly instead of the correct name “oxazoline”
- Most of the prepared compounds got abbreviations or their combinations – unfortunately, these abbreviations are not present in the Abbreviations section
- The numbering of compounds is quite inconsistent and sometimes confusing. The compound 2-a in Scheme 5 has a different structure than the compound 2-a in Scheme

7, which also somehow loses its “a” suffix in the Experimental part. The compound 2-a in the Scheme 7 has also assigned another number - 3-b; and the compound with the abbreviation HT-Br had also been assigned two different numbers (3-a, 4-b).

- If the synthesis of a compound has been already published, just reference should be given to its preparation. Eventually, for modified procedures, the reason or advantages of the used modification should be specified. For characterizations, a statement about the agreement with the published spectra would have been sufficient. In the thesis, this applies at least to compounds bzimpy-OH, BrPyMe, BrPy, BrPyCl. For the preparation of BrPyMe, almost identical synthetic procedure was published in 2007 (<https://doi.org/10.1016/j.tet.2007.10.064>) so the reference for sure should have been given.

There are also some questions for discussion:

- How many times were recorded the UV/vis and luminescence spectra used for characterization of the compounds?
- On page 39, what does the sentence "due to strong hydrophobic effect" mean? What is meant by hydrophobic effect and what it was causing?
- From how many measurements were determined the data presented in Table 8? Looking at the NMRs in Figure 21, it looks like the integrals at 2.6, which were used to determine the regioregularity, might be difficult to get reproducibly.
- For characterization of the prepared compounds were used NMR, IR and elemental analysis. Why not MS? How were the other characterization methods picked? Some compounds have just ¹H-NMR, some ¹H- and ¹³C-NMR, for some the elemental analysis is missing. More consistency would for sure look better.

Despite the above critical comments I consider the thesis to be well written and the results are interesting. Its quality was also confirmed by two papers related directly to this work, published in impacted journals, in which Sviatoslav Hladysch is the first author. Therefore, I recommend the thesis for defense.

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